

**METALLURGICAL MARVELS OF
ANCIENT INDIA**

20

DELHI IRON PILLAR



The Delhi Iron Pillar



Prof. R. BALASUBRAMANIAM

Heritage Publication Series - 49

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About the Author

Professor Balasubramaniam has vast experience in teaching corrosion and research activities related to materials-hydrogen interactions, corrosion, oxidation and failure analysis. After graduating in metallurgical engineering from the Banaras Hindu University in 1984 with a gold medal, he completed his PhD in materials engineering from Rensselaer Polytechnic Institute, USA in 1990. He has, since then, been teaching and conducting research at the Indian Institute of Technology, Kanpur in the Department of Materials and Metallurgical Engineering. He is the author of one book and more than 120 technical papers in international and national scientific engineering journals. He is the recipient of several papers in international and national scientific engineering journals. He is recipient of several prestigious awards like the BHU University Gold Medal (1984), BHU Ghandhy Gold Medal (1984), Indian Institute of Metals Vishwa Bharathi Award (1984), Indian National Science Academy Young Scientist Award (1993), Humboldt Fellowship from the German Government (1996), Materials Research Society of India Medal (1999)

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INTRODUCTION

Ancient India had a rich and vibrant cultural and scientific heritage. The pioneering ferrous and non-ferrous metallurgical traditions of ancient India have been well recognized internationally. The Delhi iron pillar is testimony to the high level of skill achieved by the ancient Indian iron smiths in the extraction and processing of iron. It has attracted the attention of archaeologists and corrosion technologists as it has withstood corrosion for the last 1600 years. It is a living testimony to the country's metallurgical pride and heritage. The first systematic scientific study of the Delhi iron pillar (DIP) was undertaken by Hadfield. There have been a growing number of studies where several aspects of the DIP have been discussed. In the centenary year of the Archaeological Survey of India in 1961, the Delhi iron pillar was studied in detail with the co-operation of the National Metallurgical Laboratory (NML), Jamshedpur. The buried underground region of the pillar was examined by archaeological excavation. Moreover, a relatively large iron sample was taken from the pillar and subjected to several metallurgical analyses at NML. The results of these scientific studies have been summarized in a special issue of the *NML Technical Journal* (Volume 5, 1963). These studies provided the firm foundation for further scientific studies of the DIP. A review of the pillar's corrosion resistance appeared 1970² and recently, the known scientific facts about the DIP have been published in the form of a book by Anantharaman³. The present booklet will briefly address the new insights on the DIP based on research carried out at IIT Kanpur under the supervision of the author. The complete details of the studies are available elsewhere⁴.

Prof. R. Balasubramanian

History : Identity of Chandra

Among the several inscriptions on the pillar, the oldest (and also the largest) is a three-stanza six line Sanskrit inscription, at a level of about 7 feet from the stone platform, which states that the pillar was erected as a lofty stand in a Vishnu temple on a hill called *Vishnupadagiri* by a king *Chandra*. The theories proposed to identify *Chandra* have been critically reviewed elsewhere⁴. Based on the nature of the Brahmi characters, the inscription must be dated between 400 and 450 AD. Therefore, the iron pillar was constructed during the rule of the Guptas in ancient India. The Gupta monarchs were Chandragupta I, Samudragupta, Chandragupta II, Kumaragupta I and Skandagupta.

In order to identify *Chandra*, numismatic evidence would be presented. The inscription clearly tells that the king had the name *Chandra* which is the most important clue to determine his identity. There are several gold coin-types in which Chandragupta II Vikramaditya's short name of *Chandra* is inscribed. This line of proof has already been stated by many commentators, which alone is not sufficient. The additional crucial argument for the unambiguous identification of *Chandra*, from numismatic sources is presented below. The most popular gold coin type which was issued by the Gupta monarchs from the time of Samudragupta was the archer type gold coin. In fact, the archer coin type seems to have been the only issue of some of the later Gupta monarchs. These coins depict the king with a bow and a short name of the issuing king. The Garuda emblem is another regular feature of these coins. The most interesting aspect about the archer coin type is that the king's short name is inscribed in the obverse field (i.e. region of the figure) with the full name and title in the circular legend. In the case of Samudragupta's archer coins, *Samudra* is found below his left arm clear of the bow. In all the types of archer gold coins of Chandragupta II, the short name of the king is inscribed as *Chandra* while the complete title and name is provided in the circular legend. Therefore, it is amply clear that

Chandragupta II, Vikramaditya was called as *Chandra* and this is attested firmly by his most popular coin-type. In the archer coins of Kumaragupta I, the name provided in the obverse field is *Kumara* or *Ku* or absent in some, but appearing as *Kumaragupta* in the circular legend. Kumaragupta's successor was Skandagupta and their line of succession is not known with certainty. However, the description of the later Gupta monarchs is provided from the archer coin types of the later Guptas⁴. Therefore, analysis of the archer coin type of the imperial Guptas provides conclusive evidence that *Chandra* was the short name of Chandragupta II, Vikramaditya⁴.

Location of *Vishnupadagiri* : Opinions vary on the identity of the *Vishnupadagiri* hill and all of them have been summarized elsewhere^{4,5,6}. We need to seek *Vishnupadagiri* in the region which was well within the territory of Chandragupta II. The centre that satisfies this important criterion is the region comprising present Udayagiri-Besnagar-Vidisha-Sanchi. The importance of this region for Vaishnavism and for the religious activities of the Guptas is attested by the fact the Guptas created their first rock-cut temples in this region, i.e. at Udayagiri. The Udayagiri cave temples also possess the unique distinction of being the only works which can be personally associated with Chandragupta II, Vikramaditya. Harle⁷ notes that "the nearest that we can actually come to visualizing an Imperial Gupta monarch is here, among the low hills and the wide plains of Central India. Chandragupta II must almost certainly have walked, surrounded by his retinue, along the narrow roads that run past the caves and made his devotions here"

The well-known and imposing of the Udayagiri sculptures are the great panel of the *Varaha* (Boar) incarnation of Vishnu designated as Cave 5. It is actually a bas-relief and the second largest one in India measuring nearly 7m by 4m. Harle rightly points out that the larger kneeling human figure in front of *Varaha* must be Chandragupta II Vikramaditya. The appearance of the object on which *Varaha* sets his foot on is more like a mountain, the living image of *Vishnupadagiri*. It must also be noticed that the

rock, on which *Varaha* sets his foot on, contains cave-like cavities carved out of the rock which is similar in appearance to the Udayagiri itself with its cave temples. This evidence very strongly suggests that the Udayagiri mountain must possibly be the *Vishnupadagiri* mentioned in the Delhi iron pillar inscription. The imagery supplied by the panel in cave 5 further strengthens this argument. It is noted that Garuda, the vahana (mascot) of Vishnu, is missing in the *Varaha* panel. There is no *garudastambha* in front of the bas-relief. The iron pillar could have formed the *garudastambha* of this temple. The language of the inscription of the Delhi iron pillar also indicate that this pillar could have been possibly located in front of the *Varaha* panel in which Chandragupta II is depicted looking up to *Varaha*. The scene depicted in the iron pillar inscription, i.e. "having in faith fixed his mind upon (the god) Vishnu", is literally presented in the *Varaha* panel.

Later History : The later history of the pillar is not known with any certainty. One group of theories ^{3,5} state that the pillar was moved from the original location and was erected in the main temple at Dhilli (Delhi), when it was developed around 1050 AD by the Tomar king Anangapala. The fortress city of Lal Kot changed hands after the defeat of prithviraj Chauhan by Qutb-ud-din Aibak in 1191 AD. Aibak erected a mosque, between 1192 and 1199 AD, called the *Quwwat-ul-Islam* (Might of Islam). The pillar currently stands in the open courtyard of this mosque, the first to be Indo-Islamic structure built in India. The mosque was built on the base of a temple that once occupied the site and constructed with materials taken from twenty seven destroyed temples in the nearby vicinity. An interesting hypothesis regarding the pillar's movement to its current location in Delhi has been advanced by Dass⁸ according to which Iltutmish moved the pillar from Malwa to Delhi, as he was the first Muslim invader to loot and plunder Malwa. In the details of Iltutmish's expedition to Malwa, which has been well documented by a contemporary historian Minhaj, mention must be made of "the effigy of Vikramjit..... together with other effigies, which were formed of molten brass,..... were

carried away to the Dhilli, the capital". The possibility of the iron pillar being one of the brass effigies carried away to Delhi exists because several earlier observers of the pillar have stated that it was made of brass⁴.

Engineering Design of Pillar : The current burial level of the pillar was not original burial level when it formed a part of the temple. Hammer-marked cavities that are still visible on the surface of the pillar in the rough region just below the smooth surface-finish region. The rough portion of the pillar was displaced from its original position. The stone platform round the base of the iron pillar was constructed in the last century by Beglar⁹. Sketches and earlier published photographs of the pillar taken before ^{10,11} attest to this.

A critical analysis of the dimensions of the main body of the pillar provided conclusive evidence for the original burial level of the pillar and also an appreciation of the pillar's symmetrical design⁵. The rough surface occupies one-fourth (60U) and the smooth surface three-fourths (180U) of the pillar, excluding the decorative top. The burial of the pillar body to one-fourth of its height would have provided the necessary stability to the structure. The decorative bell capital ¹² is again a symmetrical object. The *garuda* idol would have been approximately 20U in length thereby providing the total length of the decorative top as 60U. The length of the decorative capital (60U) would now be exactly one-fourth of the total pillar height exposed above the ground level (240U). Therefore, it is reasonable to state that the depth of burial below the ground level was equal to the height of the decorative capital, indicative of the engineering design of the pillar. The unit U is equal to 1 inch (1 *angulam*)

Composition of Delhi Iron Pillar (DIP) : Several analyses of the DIP iron composition are available ever since the first analysis was published by Hadfield¹ in 1912. The published chemical analyses ^{1, 13, 14, 15} of the DIP iron are available from which the variation in the DIP iron composition can be noted. Hadfield stressed that the composition of iron was determined by specific

analysis and not by the difference. A sample of DIP iron was also subjected to microprobe analysis in order to determine the composition of Cu (0.05%), Ni (0.05%), Mn (0.07%) and Cr (Nil) which were uniform through several millimeters in the sample from the surface¹⁶. Wranglen² utilised the available compositions (excluding that of Lal¹⁵) and estimated the average composition of the DIP iron as 0.15%C, 0.25%P, 0.005%S, 0.05%Si, 0.02%N, 0.05%Mn, 0.03% Cu, 0.05% Ni and balance Fe.

Microstructure of the Iron : The intimate relationship between structure and properties is well established in material engineering. The Delhi pillar iron possesses a non-uniform grains structure^{13,16}. In the un-etched condition, the specimens showed slag inclusions irregularly distributed in the microstructure. The etched specimens revealed medium to coarse polyhedral grains of ferrite with slip bands in some grains near the surface. The surface regions were free from pearlite which seemed to increase towards the interior. Many slip bands were seen in the surface ferrite grains. Elongated slag particles and oxide particles were also seen in the deformed structure in the near surface regions. Lahiri et al¹⁴ also conducted metallographic examination of the DIP iron and the irregular distribution of pearlite was also noted. The absence of uniform distribution of pearlite is indicative of segregation of P. In such areas of P segregation, C diffuses out and the material becomes poorer in C. But the interior portions were comparatively rich in C^{13,16}. Therefore, a wide variation in structure is exhibited in the DIP iron and this is a characteristic feature of ancient Indian iron. The non-uniform structure could be the reason for the difference in the chemical analyses of the DIP iron composition as determined by several investigators.

The DIP iron was characterized by relatively high proportion of slag inclusions. The microstructure near the slags showed wide variations (including normalised and annealed structures)¹³. Moreover, microstructures containing 0.2% to 0.3% C were present next to the slag particles, in addition to carbon-free grains. As a result of slag particles in the structure, the specific gravity of DIP iron is lower than that for the purest form of Fe.

The specific gravity is not uniform indicative of the non-uniform distribution of the slag particles in the microstructure. The non-uniform nature of the slag particles in the DIP iron can be clearly seen in the microstructures provided by Ghosh¹³, and Bardget and Stanners¹⁶. The slag present in the iron is generally microscopic in nature a few of them in larger sizes. Slag in the microstructure was due to the processing method employed to obtain iron. Iron was produced in ancient India by solid state reduction of high quality iron ore using charcoal¹⁷. Once the reduction was complete, the iron blooms produced were hammered in order to remove the liquid slag. Some of the slag particles invariably remained in the bulk of the material and this is the origin of the entrapped slag inclusions. Moreover, ancient Indian iron also shows the presence of small amounts of unreduced iron oxides. Generally, silica combined with unreduced iron oxide, results in the slag fayelite Fe_2SiO_4 . Microstructural investigations on iron produced during the Gupta period show that both slag and unreduced iron oxide were present in the main body of Eran iron^{18,19}. These unreduced iron oxides also contained carbon, presumably due the charcoal used for the extraction¹⁸. The presence of carbon in this would render these oxides cathodic in nature with respect to the surrounding matrix.

It must also be noticed that the slag particles in the DIP iron are in fine microscopic form distributed unevenly in the microstructure. Had the slag enclosed the individual iron lumps that were forge welded (in order to produce the large dimension of the pillar), it would have resulted in poor solid state fusion of the iron lumps. The pillar is a solid body²⁰ with good mechanical strength (yield strength YS of 23.5 tons per sq. in., ultimate tensile strength UTS of 23.9 tons per sq. in. and 5% elongation¹³). The relatively high strength and the similarity of YS and UTS are indicative of the composite structure of the DIP iron. In fact, a cannon ball fired at the Delhi iron pillar in the 18th century (either by Nadir Shah in 1739 AD or Ghulam Quadir in 1787) failed to break the pillar, suggesting that slag does not coat the individual lumps that were forge welded.

A very interesting feature concerning the presence of slag particles in ancient Indian iron is that they are generally surrounded by a relatively higher fraction of pearlite compared to regions far removed from the slags. This is observed in the microstructures of DIP iron¹³ and Eran iron¹⁸. The pearlite volume fraction is relatively greater near the slag particles. The presence of a larger amount of pearlite near the slag inclusions is indicative of P depletion in these regions. Chemical analysis of the P content in DIP iron has revealed that the major portion is in solid solution while a smaller amount occurs in the slags. Out of 0.28% P in the material, 0.10% P was in the fixed state, (i.e. in slags) the rest being in solid solution in the metal¹³. The presence of more pearlite near the slag inclusions has an important implication as regards understanding potential cathodic sites in ancient Indian iron (i.e. slag regions would act as cathodic reaction sites due to the large volume fraction of cementite present at these locations).

Origin of Phosphorous in Metal : It is known that the presence of P is crucial to the corrosion resistance of DIP. As the DIP iron contains a larger amount of P than modern-day iron (produced in the blast furnaces), the reason for the high P contents in the iron is briefly addressed. It was earlier believed that P in ancient steels come from slag inclusions²¹, recent developments in slag chemistry help in understanding the problem. The relatively higher P content in ancient iron is related to the kind of slag that was created in the extraction process by solid state reduction. Lime was not added in the ancient Indian furnaces, unlike in today's blast furnaces, and therefore the slag that formed in these ancient Indian furnaces were essentially fayalitic slags (i.e. consisting of iron orthosilicates, Fe_2SiO_4). This is also corroborated by available compositions of ancient iron-making slags from archaeological excavation sites¹⁵. The slags do not contain lime¹⁵. The efficiency of removal of P from the metal, which invariably must have resulted in higher P contents in ancient Indian irons. Thermodynamic analysis of P removal from iron in the absence of CaO in the slag also provides the same answer²³. As the entrapped slag seen in the ancient Indian iron is generally fayalitic

without any CaO, thermodynamics dictates that a higher amount of P should remain in solid solution in Fe. This must be one of the reasons for the presence of higher P in ancient Indian iron. It must also be noted that P addition was also intentional. For example, Buchanan²⁴, in his detailed description of steel making in Karnataka in the 18th century, describes that in one primitive furnace operated at Deveraya Durga, conical clay crucibles were filled with a specific amount of wood, from the barks of a plant *cassia auriculata*, pieces of wrought iron, then sealed and fired. The bark of this plant contains a high content of P.

Iron Manufacturing Methodology : The Iron manufacturing methodology for the main body of the pillar will be addressed initially²⁰. It should be noted that the starting material is, of course, iron lump and the method used to fuse the lumps together was forge welding. The individual iron lumps obtained from the metal extraction process had to be joined in order to produce large objects. This was accomplished by forge welding. Forge welding is an operation in which iron lumps are joined together by forging them in the hot state such that fusion is obtained between them. This process initially involves heating of the lumps to relatively high temperature in a bed of charcoal in order to make them soft and amenable for deformation. One lump is then placed on top of another and force is applied in order to weld them in the solid state. As the force is dynamic in nature, it is called forge welding.

Building the Main Body : The likely methods by which the Delhi iron pillar could have been manufactured is briefly described to provide an overview of the process. This is based on the critical analysis of the various aspects concerning the manufacturing methodology like hammering, heating, forging, use of inserts, use of dies and ease of handling²⁰. The heated iron lumps were placed on the side surface of the pillar and hammered on to the same by the use of hand-held hammers. The addition of metal would have been sideways with the pillar in the horizontal direction. The pillar's vertical and horizontal movements would have been aided by handling clamps provided on the surface of the pillar, the protruding portion of which must have been chiseled

away during the surface finishing operations. Visual proof for the presence of these clamps is available at two locations on the pillar. The first location is the previously-polished surface where the presence of a rectangular insert is seen. The region where the insert is located was previously brightly polished due to visitors clasping their hands around the pillar, before the construction of the iron cage around the pillar recently. The insert (originally containing the holding clamp) appears to have been inserted on the surface of the pillar which is indicated by the presence of cracks emanating from the insert periphery on to the surrounding lumps of iron. The second location where a handling clamp could have been present is situated approximately about one fourth of the height from the top of the main body of the pillar. There is a horizontal rectangular object currently missing from the surface at this location. Close observation of this region reveals that this rectangular slot is exactly of the same dimensions as that of the rectangular insert (i.e. the remanant of the handling clamp) seen in the bright polished region. Moreover, it occurs exactly in line with the bottom insert (i.e. it is aligned with respect to the bottom rectangular insert). The location of these inserts with respect to the pillar body dimensions should also be appreciated. The location of the top missing insert appears at a distance of (approximately 60" from the top of the pillar main body. The rectangular insert seen in the bright polished region appears at a distance of 150" from the top of the pillar main body and, therefore, 90" from the bottom of the pillar. The distance between these two inserts is 90". The body would have been rotated with the aid of rotating pegs inserted in the holes provided on the surface for this purpose. These holding supports would have aided heating the surface to be forged and then bringing this heated surface on top of an anvil. The anvil would have served additionally as a die. The hot lump to be forged is placed on top of this side section and then forged with the aid of hammers. Once a certain length of the pillar must have been manufactured, the handling of the pillar becomes more tedious and therefore to aid this process, handling clamps must have been provided on the surface of the pillar at regular intervals. The protruding portion of the insert

must have been chisled off leaving behind the remnant of the insert in the form of a rectangular block on the surface of the material. Finally, the surface of the pillar (that was supposed to be exposed) must have been smoothened by chiseling and burnishing the surface of the pillar and, thereby providing it a smooth tapered cylindrical appearance. Lastly, the Sanskrit inscriptions are inscribed on to the surface of the pillar. Cold dies must have been used for inscribing on the metal surface possibly being locally heated before inscribing. The decorative bell capital must have been finally fitted on to the top portion and then erected in the main courtyard of the Vishnu temple.

Decorative Bell Capital : The decorative bell capital consists of seven distinct parts. The bottom-most part is the reeded bell structure which has been manufactured by utilizing iron rods of uniform diameter. Atop this comes the slanted rod structure. There are several evidences at the joints between the members to indicate that lead solders were utilized for jointing the pieces together^{25,26}. The next three parts are rounded structures, with the top one being only half rounded when the pillar is viewed from the bottom, this part would appear curved. A round disc comes above this and finally the box pedestal is placed on the top of the capital. The capital contains holes that are empty at the four corners¹² and these must have been originally utilized for holding the figures of lions, based on the architecture of Gupta capitals¹². The top of the pillar presently contains a hollow slot in which an idol of Garuda must have been originally present. Individual components are shown shrunk fit around a hollow cylinder. Evidence for this kind of fitting method has been presented earlier¹². The cylinder would also have helped handling the pillar and also for joining the capital with the main body by the aid of inserts. Cross markings were observed on two of the parts and these could be related to the alignment of the individual components, although they are not strictly aligned with each other in the overall context of the decorative bell capital.

Corrosion Resistance : Several theories that have been proposed to explain the pillar's superior corrosion resistance. They can be

broadly classified into two categories: the environmental and material theories^{4, 27, 28}. The proponents of the environment theory state that the mild climate of Delhi is responsible for the corrosion resistance of the Delhi iron pillar as the relative humidity at Delhi does not exceed 70% for significant periods of time in the year. It is known that atmospheric rusting of iron is not significant at humidity levels less than 70%. Several investigators have stressed the importance of the material of construction as the primary cause for its corrosion resistance. The ideas proposed in this regard are the high purity of the iron used, presence of phosphorus and absence of S/Mn in the iron, its slag enveloped metal grain structure, passivity enhancement in the presence of slag particles and formation of phosphate film. Other theories to explain the corrosion resistance are also to be found in the literature like the mass metal effect, initial exposure to an alkaline and ammonical environment, residual compressive stresses resulting from the surface finishing (hammering) operation, freedom from sulfur contamination both in the metal and in the air, presence of layers of cinder in the metal thereby not allowing corrosion to proceed beyond the layer (cinder theory) and surface coating provided to the pillar after manufacture (treating the surface with steam and slag coating) and during use (coating with clarified butter, painting). The material of construction may be the important factor in determining the corrosion resistance of the ancient Indian iron is attested by the presence of ancient massive iron objects located in areas where the relative humidity is high for significant periods in the year (for example, the iron beams in the Surya temple at Konark in coastal Orissa and the iron pillar at Mookambika temple at Kollur situated in the Kodachadri Hills on the western coast). It is, therefore, obvious that the ancient Indians, especially from the time of the Guptas (300-500 AD), produced iron that was capable of withstanding corrosion. This is primarily due to the high P content of the iron produced during ancient times.

Beneficial Role of Slag Particles in the Passivation Process: The presence of the second phase particles in the microstructure would

result in the creation of mini-galvanic corrosion cells when the iron is exposed to the environment. Relatively high corrosion rates was observed experimentally in the initial exposure period of Eran iron compared to mild steel of similar C content¹⁸. Therefore, it is anticipated that the two-phase structure of the DIP iron should corrode at a faster rate compared to iron of similar composition as the DIP iron is essentially a composite structure.

In order to explain the anomaly of the composite structure DIP iron exhibiting excellent corrosion resistance, the oxidation and reduction processes occurring on the P-containing DIP iron were analysed using the mixed potential theory²⁷⁻²⁹. Potentiodynamic polarisation studies conducted on phosphated steels reveal that the critical current density for the formation of the phosphate layer can be higher by more than three order of magnitude compared to that for steel without P²⁹. Therefore, it is valid to indicate that the DIP iron will exhibit active-passive behaviour on anodic polarisation. It is important to stress that the exact nature of the passive film need not be known for this theoretical analysis and only the formation of passive film is required while considering the mixed potential analysis.

In case the DIP iron did not contain slag particles, the cathodic activation polarisation line would have intersected the anodic polarisation curve in the or the passive active region. The relatively large currents needed to induce passivity in iron containing P must be noted. However, in the presence of slag particles, the exchange current of the cathodic reaction(s) would be higher and the cathodic activation polarisation line would shift to the right. Therefore, the critical current density for the formation of the passive film should be attained. Once this is achieved, the passive film covers the surface and the corrosion rate is reduced to low rates. Therefore, the presence of slag particles may be indirectly beneficial in the case of DIP iron as it helps in the induction of passivity on the surface. The above mixed potential analysis was experimentally validated by potentiodynamic polarisation studies using ancient Indian iron of different slag

contents^{27,28}. The corrosion resistance of the Delhi iron pillar, therefore, has theoretical support.

Although the above discussion clearly establishes that the second phase particles in the DIP iron may be beneficial in inducing passivity, it should be borne in mind that alternate wetting and drying conditions are implied while considering atmospheric corrosion. As shall be presented later, this is a very important factor in formation of the protective film at the metal-metaloxide interface. In case iron with such second phase particles (slags and oxides) is exposed to a more severe environment, for example complete immersion in acidic or alkaline solution, rapid localised attack occurs at the second phase-matrix interfaces, and the material, corrodes at a much faster rate than normal mild steel. This has also been experimentally validated for ancient Indian iron by constant immersion corrosion testing and microstructural examination using a scanning electron microscope¹⁸. In the case of DIP iron, the importance of alternate wetting and drying conditions for its corrosion resistance can be gleaned by analysing the available corrosion rate data. Incidentally, the rust growth kinetics on the DIP has been analyzed in detail, elsewhere³⁰. Wranglen² utilised the weight loss data to estimate the thickness of protective film that forms on the surface of the DIP. Assuming parabolic growth kinetics, he predicted the thickness of the scale to be 200 μm after about 1600 years of growth. The excellent match of the estimated thickness with that experimentally estimated by Bardgett and Stanners¹⁶, using a permanent magnet type thickness gauge, was indicated as proof that the film that forms on the surface is protective in nature as it grows according to parabolic kinetics. It is interesting at this juncture to note that the corrosion rates determined by constant immersion testing of DIP iron samples in 0.001% NaCl and 0.003% SO_2 solutions were 6mg/sq cm/day (mdd) and 54 mdd, respectively¹³. Utilising these values, it can be easily seen that had the pillar been completely immersed in an aqueous solution, it would have been corroded much more severely.

Delhi Iron Pillar Rust Characterization : Rust samples were characterised by XRD³¹, Fourier Transform Infrared (FTIR) spectroscopy³² and Mossbauer spectroscopy³³. The salient results of the characterisation studies are summarised below. It must be again emphasised that the rust samples were obtained from the region just below the decorative bell capital and therefore, this must be the oldest rust on the pillar as the area from where the rust was collected is inaccessible to the public.

The significant result of the XRD analysis of the DIP rust was the identification of iron hydrogen phosphate hydrate in the crystalline form. The FTIR spectroscopic study of the DIP rust clearly established that, in addition to iron hydrogen phosphate hydrate, the scale also consisted of γ -FeOOH (lepidocrocite), α -FeOOH (goethite), δ -FeOOH (misawite), magnetite and phosphates. The hydrated nature of these products was also indicated. It was also seen in the XRD pattern that there was a very small amount of iron oxide/oxyhydroxides present in the crystalline form. The identification of the oxide/oxyhydroxides of iron by FTIR clearly established that they are present in the amorphous form. The FTIR study also provided that phosphate ions were present in the rust, confirming the results of XRD. The Mossbauer spectroscopic study of the DIP rust samples proved conclusively that the oxyhydroxides and magnetite were present in the amorphous form, and also that iron in the phosphate was in the +3 oxidation state. In summary, the XRD analysis proved the presence of crystalline iron hydrogen phosphate hydrate, FTIR and Mossbauer spectroscopy proved the presence of magnetic and other oxyhydroxides in the amorphous form.

In order to understand the presence of the identified corrosion products in the DIP rust, the stabilities of these compounds were compared. The free energy of formation of the oxides and oxyhydroxides of iron, iron phosphate and phosphoric acid are provided³⁴. Among the compounds listed in the table, the phosphates are very stable based on their relatively large negative values of free energy of formation. This has also been verified by noting that in the ternary Fe-P-O phase diagram, the

formation of phosphate is favourable even when only 0.24%P is present.

Process of Protective Rust Formation: The process of protective film formation on the expected surface of the Delhi iron pillar can be outlined based on the detailed characterization of the rust. It must be remembered that alternate wetting and drying conditions are implicit in the following discussion on atmospheric corrosion.

Initially, the corrosion of the matrix is relatively fast due to the presence of second phase particles in the microstructure. The usual corrosion products that are observed in the case of mild steels (exposed to atmosphere containing no chloride ions) are generated. It is well known that the corrosion products that form on iron on atmospheric exposure are α - FeOOH (goethite), γ -FeOOH (lepidocrocite), $\text{Fe}_{3-x}\text{O}_4$ (magnetite) and x-ray amorphous matter^{35,36}. In case of exposure in marine environments (i.e. where chloride ions are present), the formation of β -FeOOH (akaganeite) is favoured. In the case of DIP iron, the formation of lepidocrocite and goethite was confirmed by XRD analysis of 1.5 year old rust from the Delhi iron pillar surface by Lahiri et al¹⁴.

The initial enhanced corrosion of the matrix leads to the enrichment of P concentration at the metal-scale interface between the metal and rust, the formation of the compact layer of amorphous δ -FeOOH layer next to the metal-metaloxide interface should be favoured like that observed in the case of P-containing weathering steels. Moreover, experiments have shown that H_2PO_4 ions prevent crystal growth of the corrosion products. The formation of amorphous δ -FeOOH confers the initial corrosion resistance to the DIP iron. The δ -FeOOH phase forms in a discontinuous manner in normal mild steel while it forms as a compact layer next to the metal-metaloxide interface in the case of P- or Cu- containing weathering steels. It has been attributed to this compact δ -FeOOH layer next to the metal surface, which is also enriched with the element(s) added to provide weathering resistance (i.e. Cu and P).

It is important to note that the oxyhydroxides and magnetite present in the old DIP rust are nanocrystalline/amorphous in nature and not crystalline. As it is known that the initial oxide and oxyhydroxides that form on the DIP iron are crystalline in nature¹⁴, the long-term conversion of the crystalline forms of these oxyhydroxides to the amorphous form is indicated. The crystalline oxide/oxyhydroxides of iron are converted to the amorphous state due to process of alternate wetting and drying, as has been shown in P-containing weathering steel³⁵.

The enrichment of P in the δ -FeOOH layer continues with prolonged exposure and this has been observed in P-containing weathering steels^{35,36}. This enrichment should be responsible for the precipitation of the insoluble phosphate identified by XRD. The process of formation of crystalline iron hydrogen phosphate hydrate would be understood based on the vast literature available on phosphating of steels³⁸. This exercise would also be useful in further understanding the reason for the Delhi iron pillar's excellent corrosion resistance.

Phosphating of iron is a commercially important coating method which involves the formation of relatively insoluble, electrically non-conducting thin films of metallic phosphates on the surface. It is known that the formation of a protective layer on Fe surface involves the following four steps³⁸. In the first step, electrochemical attack of iron by orthophosphoric acid occurs over a wide range of concentration and temperature. In the case of DIP iron, the formation of orthophosphoric acid next to the metal surface has to be first understood. The enrichment of P at this location was earlier established due to the initial corrosion of matrix. However, it is also important to note that the concentration of P is relatively higher near the surface regions than in the bulk¹³. It is known that P diffuses and concentrates in regions where C is depleted and therefore, concentration of P is relatively higher near the surface regions of the pillar. Therefore, enrichment of P in the δ -FeOOH layer is expected.

This P enrichment has been experimentally determined by Ghosh¹³ who mentioned that the P content in the DIP rust was 0.35% whereas the P content in the DIP iron was 0.18%. The enrichment of P in the rust would initially result in the formation of phosphoric acid at the metal-metaloxide interface due to the presence of P at this location and also as free energy consideration favour its formation. The moisture for phosphoric acid formation obtains in the alternate wetting and drying cycles. In contact with phosphoric acid, the dissolution potential of iron becomes less and it causes the dissolution of Fe to sparingly soluble dihydrogen phosphate according to



The transient oxides of iron (in which Fe is in the +2 oxidation state) will also be corroded by phosphoric acid to provide $\text{Fe}(\text{H}_2\text{PO}_4)_2$ according to



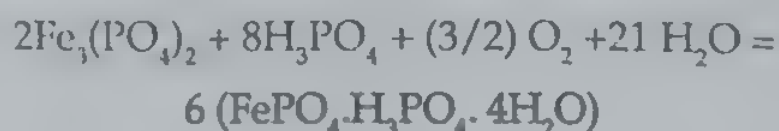
Among the above two reactions, the first one mainly occurs³⁸.

In the second stage, the contact of the metal shifts the equilibrium in such a way that massive precipitation of monohydrogen phosphate FeHPO_4 and tribasic iron phosphate $\text{Fe}_3(\text{PO}_4)_2$ occurs.

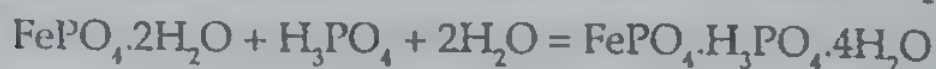
Both these phosphates are insoluble in nature. Moreover, these phosphates are also amorphous in nature and this is well corroborated by experimental evidence.

In normal conditions, the phosphating reactions generally discussed are up to the sequence of events provided above. In normal practice, other cations such as Zn or Mn are also added to phosphoric acid. In some cases, oxidising agents are added so that iron may appear in the coating as ferric phosphate. This has been proved to be more beneficial to corrosion resistance as the crystal reorganisation of the amorphous phosphates to phosphates results in a large reduction in the porosity of the phosphates and subsequently, much protective properties.

The oxidation of iron to ferric phosphate can also be achieved by alternate wetting and drying cycles. The H_2PO_4^- ions accelerate the air oxidation of Fe^{2+} to Fe^{3+} under alternate wetting and drying cycles and also prevent the crystal growth of the corrosion products. Over time, $\text{Fe}_3(\text{PO}_4)_2$ is oxidised by atmospheric oxygen and H_3PO_4 to iron hydrogen phosphate hydrate.



In this compound, iron is in the +3 state and this can be understood if one considers the above reaction in parts as follows:



The dissolution and reprecipitation reaction also leads to a change in the pH of the metal-solution interface, which leads to crystalline reorganisation and followed, most importantly, by a large decrease in porosity. The crystalline reorganisation is a very deep-seated reaction (at the metal-phosphate interface) which modifies the porosity of the passive layer and decreases markedly the exposed metallic surface³⁸. Therefore, the formation of the crystalline iron hydrogen phosphate hydrate from the amorphous phosphate is critical in providing excellent protection against moisture and oxygen to the metal surface.

The continuous layer of crystalline iron hydrogen phosphate hydrate (formed at the metal metaloxide interface) is, therefore, responsible for the superior corrosion resistance of the Delhi iron pillar. Ghosh stated that "P accumulated in a new phase at the base of the main oxide film was not formed, the metal behaviour was similar to that of exposure surface of ordinary irons". Ghosh performed some simple experiments with the DIP influence of P on rusting. The sample was polished and allowed to rust. When a thin and unequally distributed film of rust was formed, it was photographed and slightly polished to remove the rust from the surface. This surface was treated with Stead's

solution to observe the distribution of P on the surface. It was found that P was generally low in the areas where rust appeared more intensely.

It is important to note that the crystalline modification of iron hydrogen phosphate hydrate was obtained in the XRD analysis³¹, indicating that the phosphate in the rust is relatively old. This validates the statement that DIP rust must be the oldest rust on the pillar as it was obtained from a region inaccessible to the public (i.e. the region just below the decorative bell capital).

Alternate wetting and drying conditions play an important role in the case of atmospheric corrosion of the DIP because they accelerate the precipitation of the protective crystalline phosphate and the amorphization of the DIP rust. The amorphization of rust is also aided by the presence of H_2PO_4 ions. The iron pillar's weight is estimated to be approximately 7 tonnes and therefore, the large mass of the metal plays a contributory role in aiding the alternate wetting and drying process. Sanyal and Preston³⁹ and, later, Bardgett and Stanners¹⁶ proposed that the large mass of the pillar implies a large shear capacity for the iron and therefore, the pillar will heat up faster or cool down faster than the surroundings. This provides the right conditions of alternate wetting and drying of the iron pillar surface. The intensity of wetting and subsequent drying would be much more in case of DIP iron because of the large mass of the pillar.

In summary, the phosphate film theory originally presented by Ghosh¹³ and elaborated in detail later by Balasubramaniam²⁷⁻²⁹ is valid, with the minor difference being that it is the crystalline (and not amorphous as originally proposed by Balasubramaniam^{27,28}) iron hydrogen phosphate hydrate layer that is responsible for the corrosion resistance of the Delhi iron pillar. The conclusion drawn is unambiguous as it has strong experimental support from actual Delhi iron pillar rust characterization.

Difference with Corrosion of Steel and Weathering Steels : The protective passive film that form on the DIP would be contrasted with the films forming on mild and weathering steel on atmospheric exposure. The rusting of normal mild steel and weathering steel is first addressed. When iron is exposed to the environment, the first oxides that form are the oxyhydroxides of Fe which oxidises from Fe(II) complexes³⁵. The first oxyhydroxide to form is lepidocrocite (γ -FeOOH). A part of it then transform to another allotropic modification (α -FeOOH) and the rust at later times is composed of both these oxyhydroxides. Both these oxyhydroxides are not protective against corrosion as they readily crack allowing for ingress of oxygen and moisture to reach the metal surface and cause further corrosion. However, with time, a part of the FeOOH formed transforms to magnetic oxides of iron, which are much more protective than these oxyhydroxides. In addition to α - and γ -FeOOH, there can be another oxyhydroxide of nature - δ -FeOOH, which can form on atmospheric exposure of iron. It is interesting to note that δ -FeOOH is generally amorphous in nature and therefore no diffraction peaks would be observed from this phase³⁵. In ordinary mild steels, this phase does not form as a continuous layer but rather in a discontinuous manner as it results due to dehydration - oxidation of the Fe (II) complexes. Therefore the δ -FeOOH that forms in ordinary mild steels is not protective in nature for these reasons. However, it is possible for this δ -FeOOH to form next to the metal surface as a continuous layer in which case the steel obtains corrosion resistance, as the oxyhydroxide is also amorphous and compact in nature. The formation of δ -FeOOH as a continuous layer next to the metal surface is catalysed by the presence of P and Cu in material³⁵. Moreover, the δ -FeOOH is enriched with P and Cu, elements that are added for improving atmospheric corrosion³⁵. The presence of this amorphous layer is the reason for the excellent corrosion resistance of the weathering steels although the time required for forming the protective layer is determined by the exposure

conditions. Several schemes for the formation of rust on steel as a function of pH and environmental factors are available^{35,36}.

In the case of DIP, the process of protective rust formation has been outlined in great detail. Cross Sectional microstructural analysis of DIP rust confirms the structure of DIP rust presented²⁹. The initial fast rate of corrosion is aided by the entrapped slag inclusion and this results in enrichment of P at metal-scale interface which promote protective film formation processes (catalytic formation of δ -FeOOH and Phosphates), thereby reducing the corrosion rate. Growth rates have been roughly estimated for these two regions based on available DIP rust thickness measurements³⁰.

Summary : New insights on the Delhi iron pillar have been discussed in this communication. The identity of *Chandra* and *Vishnupadagiri* of the oldest Sanskrit inscription on the pillare has been analyzed to show that chandra should be identified with Chandragupta II Vikramaditya while *Vishnupadagiri* should be identified with modern Udayagiri. The engineering design of the pillar was next discussed paving the decorate bell capital. The paper also briefly addressed the nature of iron that makes up the DIP and the possible reason for its relatively high P content. The nature of the protective passive layer on the corrosion resistant Delhi iron pillar (DIP) has been addressed based on details characterization of its rust. The rust was composed of iron hydrogen phosphate hydrate ($\text{FePO}_4 \cdot \text{H}_3\text{PO}_4 \cdot 4\text{H}_2\text{O}$) in the crystalline form from the addition of α - γ - δ FeOOH and magnetite, all in amorphous forms. The process of protective rust formation on DIP iron has been outlined based on the rust analysis. The passive film formation on the Delhi iron pillar has been contrasted with rusting of normal and weathering steels. The critical factor aiding the superior corrosion resistance of the Delhi iron pillar is the formation of crystalline iron hydrogen phosphate hydrate, as a thin layer next the metal-metaloxide interface, which drastically

lowers the rate of corrosion due to its low porosity content. The process of protective crystalline phosphate formation is aided by alternate wetting and drying cycles, which is the important contribution of the atmosphere to the DIP's corrosion resistance. Therefore, the corrosion resistance of the Delhi iron pillar is due to both Delhi (with the environment providing alternate wetting and drying conditions) and iron (with its high P content conferring protection by the formation of the crystalline iron hydrogen phosphate).

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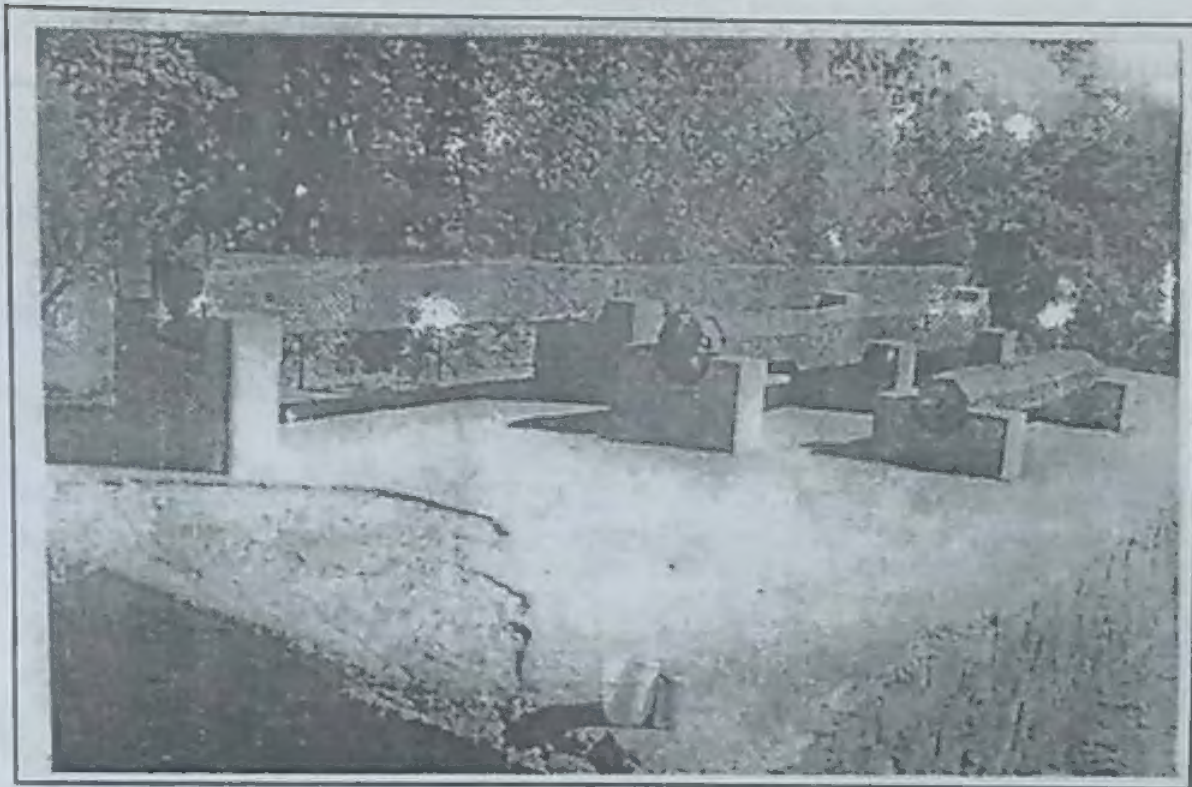
Decorative bell capital of the
Delhi iron pillar -
Top portion



Decorative bell capital of the
Delhi iron pillar -
Bottom portion

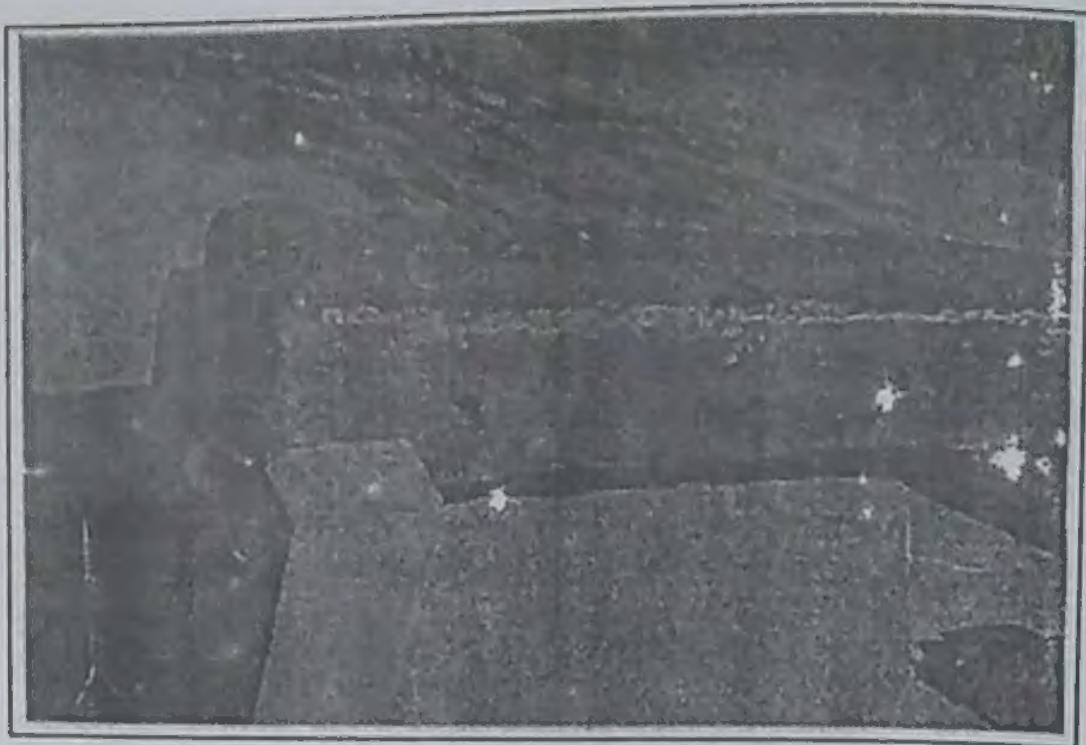


The Delhi Iron Pillar



The three pieces of the Dhar iron pillar. The longest piece is of square cross section, while the second changes from a square to octagonal and the third piece is octagonal throughout.

Dhar is situated near Indore, in Madhya Pradesh. The city was founded by King Bhoja (1010-1053 AD). Dhar could probably be the original location of the pillar which was founded by Raja Bhoja. The total length of Dhar pillar 42 feet, but it is currently lying in three broken pieces in front of the Lat Masjid of Dhar.



Hollow holes in the bottom region of the Dhar iron pillar. These hollow slots were used for gripping the pillar to the basement by means of inserts and ropes.

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